

## Chromium(III) Based Ziegler-Natta Catalysts for Olefin Polymerization (Mangkin Ziegler-Natta Berasaskan Kromium(III) untuk Pempolimeran Olefin)

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### ABSTRACT

Four chromium based oxo-trinuclear carboxylate complexes were prepared by reacting chromium(III) nitrate nonahydrate with acetic acid and substituted carboxylic acids. They were characterized using infrared spectroscopy (FT-IR). Chromium content of the complexes was determined by titrimetry method. The chromium(III) monochloroacetate complex,  $[Cr_3O(ClCH_2COO)_6 \cdot 3H_2O]NO_3 \cdot 3H_2O$  in combination with diethylaluminium chloride formed heterogeneous catalyst system for ethylene polymerization. Both Al/Cr ratio and temperature influenced the catalytic activity. The maximum activity was 1768 gPE/gCr/hr/atm, achieved by polymerizing at 29°C and monomer pressure around 1 atm, with Al/Cr ratio 30.8. Effect of chloro-substituent groups on carboxylic ligand was studied by comparing the catalytic activities of chromium(III) monochloroacetate, chromium(III) dichloroacetate, chromium(III) trichloroacetate and chromium(III) acetate. The polymerization reaction was found to be first order with respect to the monomer during the initial stage. The activity decreases very rapidly presumably due to fast decay of the active sites. The polyethylene was characterized using FT-IR and DSC, and the results showed that it was of high density and crystallinity.

*Keywords:* Chromium based complexes; ethylene polymerization; Ziegler-Natta catalyst

### ABSTRAK

Empat kompleks kromium berasaskan okso-trinuklear karboksilat telah dihasilkan melalui tindak balas antara  $Cr(NO_3)_3 \cdot 9H_2O$  dengan asid asetik dan asid karboksilik tertukarganti. Kompleks kromium yang disediakan telah dikaji dengan spektroskopi inframerah dan kaedah penitratan. Kompleks kromium(III) mono-kloro asetat  $[Cr_3O(ClCH_2COO)_6 \cdot 3H_2O]NO_3 \cdot 3H_2O$  bergabung dengan di-etilaluminium klorida untuk membentuk sistem mangkin heterogenous bagi pempolimeran etilena. Aktiviti pemangkinan dipengaruhi oleh nisbah Al/Cr dan suhu. Aktiviti maksimum bagi pempolimeran etilena tercapai apabila suhu pempolimeran adalah 29°C dan nisbah Al/Cr 30.8, iaitu 1768 gPE/gCr/j/atm. Faktor pengaruh kumpulan kloro tertukarganti pada ligan karboksilat telah dikaji dengan menggunakan kompleks kromium(III) di-kloro asetat, kromium(III) tri-kloro asetat dan kromium(III) asetat sebagai mangkin. Pempolimeran etilena dalam kajian ini adalah linear terhadap etilena pada permulaan tindak balas. Plot aktiviti lawan masa tindak-balas menunjukkan graf jenis lengkung menurun. Polietilena yang dihasilkan dikaji dengan FT-IR dan DSC dan keputusan menunjukkan bahawa polietilena yang terhasil mempunyai darjah ketumpatan yang tinggi.

*Kata kunci:* Kompleks berasaskan kromium; mangkin Ziegler-Natta; pempolimeran etilena

### INTRODUCTION

Polyethylene is a versatile polymer that offers high performance relative to other polymers. There are three main types of PE, namely the high density polyethylene (HDPE), low density polyethylene (LDPE) and linear low density polyethylene (LLDPE). Polymerization of ethylene could be carried out by both homogeneous and heterogeneous catalysts. A homogeneous catalyst is in the same phase as the medium of polymerization. Examples of homogeneous catalyst include vanadium based catalyst and metallocene catalyst. A heterogeneous catalyst is in a different phase from the medium of reaction; an example would be titanium based catalyst. Chemical reaction occurs on the surface of a heterogeneous catalyst. Usually the catalyst is in a solid phase while the reactant is a liquid or gas.

Commercially important catalysts for the polymerization of ethylene can be divided into four main categories: (1)

Philips catalysts, (2) molybdenum oxide catalysts, (3) metallocene catalysts and (4) Ziegler-Natta catalyst. Philips catalysts (McDaniel & Welch 1983) or the so called chromic catalysts are prepared by impregnating 1 to 3 percent of chromic oxide on support such as silica or silica-alumina. It yields bimodal polyethylene with good mechanical properties and good processability. Philips catalyst is the best-known chromium based commercial catalyst which has been used in more than 60% of the world's production of high density polyethylene. Molybdenum catalysts have been described as hydroforming catalysts which contain up to 8 percent of molybdenum oxide supported on alumina (Othman 2004). The catalysts are mainly used in solution process and polyethylene produced by this catalyst has an unannealed density of 0.958 to 0.960 g cm<sup>-3</sup>. Metallocene catalysts (Scheirs 2000) are based on metallocene of group 4 transition metals with methylaluminumoxane

(MAO). The catalysts exhibit a high activity for olefin polymerization and this catalyst system allows properties of the polymer produced to be tailored made in many ways. The custom properties include greater stiffness and impact strength, greater stretch and improved sealability. Although metallocene catalysts show many advantages, the polymers produced have a very narrow molecular weight distribution. A Ziegler-Natta catalyst is formed by reacting a metal alkyl or alkyl halide (often called a cocatalyst) with a transition metal salt (Boor 1979; Sinn & Kaminsky 1980; Keii 1972). Most polymers produced using heterogeneous Ziegler-Natta catalysts are with broad molecular weight distribution. Most of the Ziegler-Natta polymerization reactions are based on titanium catalyst systems. Chromium salts have been found to have very low catalytic activity in ethylene and propylene polymerization. Among those were chromium chloride,  $\text{CrCl}_2$ , chromium(III) chloride,  $\text{CrCl}_3$  and chromium acetate,  $\text{Cr}(\text{acac})_3$ .

Recently Batelle patented a chromium based Ziegler-Natta catalyst,  $(\text{Cr}(\text{CH}_3\text{COO})_3)$  which was prepared from chromium acetate and acetic anhydride. When combined with diethylaluminium chloride ( $\text{AlEt}_2\text{Cl}$ ), this catalyst gave a very high activity in ethylene polymerization. Later, Gan et al. (1987) reported that the same catalyst could be prepared by different starting materials. They had used the catalyst for both the homopolymerization and random copolymerization of ethylene and propylene. In this study, chromium based oxo-trinuclear carboxylate complexes with the general formula  $[\text{Cr}_3\text{O}(\text{RCO}_2)_6\text{3H}_2\text{O}]^+$  where R=alkyl or substituted-alkyl were synthesized. The prepared catalysts were used in ethylene polymerization using a gas line with constant volume set-up.

#### EXPERIMENTAL DETAILS

Commercial chromium(III) nitrate nonahydrate, solvents and carboxylic acids used in the synthesis of catalysts were purchased from Merck. The chemicals and solvents were analytical grade and were used as received. All the glassware was cleaned thoroughly before used. Flat bottom flasks and magnetic stirrers were kept in the drying oven to remain dryness. Chromium(III) oxo-trinuclear carboxylate complexes were synthesized by reacting chromium(III) salts of nitrate with an excess of carboxylic acids (Aishah 1995; Ooi 1996). The chromium complexes were titrated against standardized sodium thiosulphate solution. From the molar concentration of chromium solution obtained by titration, the chromium content in each complex can then be calculated. FT-IR spectra were recorded on a Perkin Elmer Spectrometer model 1600. The chromium complex was mixed with KBr powder and pressed into disc. The spectra were scanned in the range of 400-4000  $\text{cm}^{-1}$ .

High purity ethylene (99.9%) was purchased from Malaysian Oxygen Ltd Company. Analar grade toluene was purchased from MERCK and was purified by distilling over sodium metal under  $\text{N}_2$  atmosphere.  $\text{AlEt}_2\text{Cl}$  obtained from Aldrich Chemical Company was used as cocatalyst. All glassware, syringes and needles were soaked overnight

in a solution made up of potassium hydroxide and isopropyl alcohol and then cleaned thoroughly in an ultrasonic bath (Sonorex, model no. RK100) for at least 15 min. They were dried in oven at 120°C after washing and rinsing with distilled water. The gas line was evacuated and flushed with ethylene gas prior to polymerization. Ethylene polymerization was carried out at room temperature using a gas line with a constant volume set-up. Chromium(III) monochloroacetate complex was used as catalyst. About 0.02 g complex was weighed and was transferred into a 250 mL round bottom flask. The reaction flask was then loaded with toluene (solvent) followed by the required amount of  $\text{AlEt}_2\text{Cl}$  (cocatalyst). Total volume of the solvent and cocatalyst was maintained at 100 mL. The mixture was left to 'age' for 15 min before introducing the monomer gas. The rate of polymerization was monitored by reading the monomer pressure drop using mercury manometer in units of cmHg. The polymerization reaction was carried out for 1 h. At the end of the polymerization run, the reaction vessel was disconnected from the gas line. The product was poured into 400 mL methanol acidified with 5 mL concentrated hydrochloric acid in order to quench the reaction. The mixture was left to stir for a few hours. Later, the polymer precipitate was filtered with a sintered glass and was thoroughly washed with methanol. The product was then dried overnight in vacuum oven at 60°C. Polymer samples were pressed into thin film by Carver hot press at temperature between 100°C and 130°C for 20-30 s. The samples were mounted onto a cardboard holder and their spectra were recorded by Perkin-Elmer Spectrum RX1 FT-IR spectrophotometer within the range 500-4000  $\text{cm}^{-1}$ . The recorded spectra were then analyzed by Perkin-Elmer FT-IR software. Polymer samples (2-3 mg) were encapsulated in an aluminium sample pan and their weight was recorded. Calorimetric measurements for the samples were obtained using a Perkin-Elmer Differential Scanning Calorimeter, DSC 7. Useful information such as enthalpy change ( $\Delta H$ ), melting temperature ( $T_m$ ) and crystallization temperature ( $T_c$ ) of polymers can be obtained from DSC thermogram.

#### RESULTS AND DISCUSSION

Table 1 summarizes the reaction conditions to obtain optimum yield for each complex. Meanwhile, Table 2 shows the percentage of chromium contained in each catalyst. The obtained results are in well agreement with the proposed formula.

Absorption bands were assigned based on the information provided by previous works (Aishah 1995; Ooi 1996) and comparisons with the fundamental vibration frequencies of known carboxylate compounds (Bellamy 1959; Johnson et al. 1981; Nakamoto 1986). Band assignments of the corresponding complexes are listed in Table 3. All four spectra showed characteristic peaks of water of crystallization and coordination water in the range of 3568-2962  $\text{cm}^{-1}$ . Strong and broad absorption bands in this region indicated the symmetric and antisymmetric OH stretching (Nakamoto 1986) of water molecules. C-H

TABLE 1. Refluxing time and reagents ratios for optimum yield

Complex	Ratio of chromium(III) nitrate to carboxylic acid	Refluxing time/hr	Yield/g	Percentage yield /%
$[\text{Cr}_3\text{O}(\text{ClCH}_2\text{COO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot 3\text{H}_2\text{O}$	1:16	15	8.30	95.0
$[\text{Cr}_3\text{O}(\text{Cl}_2\text{CHCOO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot \text{H}_2\text{O}$	1:13	15	7.53	84.2
$[\text{Cr}_3\text{O}(\text{Cl}_3\text{CCOO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot 2\text{H}_2\text{O}$	1:6	10	9.82	90.8
$[\text{Cr}_3\text{O}(\text{CH}_3\text{CCOO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot 7\text{H}_2\text{O}$	1:13	13	5.77	92.4

TABLE 2. Comparison of  $\text{Cr}^{3+}$  content obtained from titration with theoretical values

Complex	Theoretical %Cr	Experimental %Cr	Catalyst formula
Chromium (III) monochloroacetate	17.28	17.25	$\text{Cr}_3\text{O}(\text{ClCH}_2\text{COO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot 3\text{H}_2\text{O}$
Chromium (III) dichloroacetate	14.53	14.55	$[\text{Cr}_3\text{O}(\text{Cl}_2\text{CHCOO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot \text{H}_2\text{O}$
Chromium (III) trichloroacetate	12.01	12.04	$[\text{Cr}_3\text{O}(\text{Cl}_3\text{CCOO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot 2\text{H}_2\text{O}$
Chromium (III) acetate	20.31	20.39	$[\text{Cr}_3\text{O}(\text{CH}_3\text{CCOO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot 7\text{H}_2\text{O}$

TABLE 3. FT-IR band assignments of Cr(III) complexes

Band Assignments ( $\text{cm}^{-1}$ )	Complexes			
	1	2	3	4
$\nu(\text{H}_2\text{O})$	2967-3452 <i>b</i>	2962-3568 <i>b</i>	3012-3547 <i>b</i>	3015-3539 <i>b</i>
$\nu(\text{CH})$				
$\nu_{\text{asym}}(\text{COO}^-)$	1611 <i>s</i>	1647 <i>s</i>	1667 <i>s</i>	1679 <i>s</i>
$\nu_{\text{sym}}(\text{COO}^-)$	1457 <i>s</i>	1438 <i>s</i>	1428 <i>s</i>	1428 <i>s</i>
$\nu_{\text{asym}}(\text{NO}_3^-)$	1385 <i>s</i>	1384 <i>s</i>	1384 <i>s</i>	1384 <i>s</i>
$\nu(\text{C-O})$	1298 <i>w</i>	1267 <i>m</i>	1234 <i>m</i>	1313 <i>m</i>
$\nu_{\text{sym}}(\text{NO}_3^-)$	1038 <i>m</i>	1037 <i>w</i>	1039 <i>w</i>	1040 <i>w</i>
$\nu(\text{C-Cl})$	-	801 <i>m</i>	826 <i>s</i>	791 <i>m</i>
			861 <i>s</i>	832 <i>m</i>
$\nu(\text{M-H}_2\text{O})$	700 <i>m</i>	702 <i>m</i>	726 <i>m</i>	757 <i>m</i>
$\delta(\text{COO}^-)$	677 <i>m</i>	660 <i>m</i>	662 <i>m</i>	691 <i>m</i>
$\nu_{\text{asym}}(\text{Cr}_3\text{-O})$	664 <i>m</i>	652 <i>m</i>	647 <i>m</i>	640 <i>m</i>
$\pi(\text{COO}^-)$	623 <i>m</i>	549 <i>m</i>	534 <i>m</i>	585 <i>m</i>

stretching mode appeared in the range of 3050-2940  $\text{cm}^{-1}$  (Bellamy 1959). Absorption of the free carboxylic acid was not detected in all the spectra. Instead, two strong bands of asymmetric and symmetric bridging carboxyl ( $\text{COO}^-$ ) stretching absorption were observed at around 1679-1611  $\text{cm}^{-1}$  and 1457-1428  $\text{cm}^{-1}$ . Nitrate anion gave rise to two absorption bands in the spectra (Gatehouse et al. 1957; Newman & Halford 1950) at 1385-1384  $\text{cm}^{-1}$  due to  $\nu_{\text{asym}}(\text{NO}_3^-)$  and 1037-1040  $\text{cm}^{-1}$  due to  $\nu_{\text{sym}}(\text{NO}_3^-)$ . Medium band observed at 801  $\text{cm}^{-1}$  in the spectrum of Cr(III) monochloroacetate sample corresponds to the stretching of C-Cl (Herzberg 1945; Randall et al. 1949). For Cr(III) dichloroacetate and Cr(III) trichloroacetate complexes, two C-Cl stretching peaks were observed. Splitting of the C-Cl stretching frequency into two might be due to the different conformations which are possible (Pavia 2009). Absorption at 700  $\text{cm}^{-1}$  in Cr(III) acetate has been assigned to  $\nu(\text{M-H}_2\text{O})$ . The mono-, di- and trichloro acetate

complexes show  $\text{OH}_2$  rocking absorption at 702, 726 and 757  $\text{cm}^{-1}$  respectively. Infrared absorption in the region of 691-660  $\text{cm}^{-1}$  was attributed to the symmetric O-C-O deformation mode. Johnson et al. (1981) assigned the band at 673  $\text{cm}^{-1}$  to  $\delta(\text{COO}^-)$  for  $[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot x\text{H}_2\text{O}$  complex. Assignment for asymmetric stretching frequencies of  $\text{Cr}_3\text{O}$  was complex due to the absorption by coordinated ligands in the same region (Nakamoto et al. 1961).  $\nu_{\text{asym}}(\text{M}_3\text{-O})$  are expected to lie in the region of 700-500  $\text{cm}^{-1}$ . Chromium complexes synthesized showed  $\nu_{\text{asym}}(\text{Cr}_3\text{-O})$  absorption at 664-640  $\text{cm}^{-1}$ . Absorption band in the region of 623-585  $\text{cm}^{-1}$  in four spectra were assigned to  $\pi(\text{COO}^-)$ .

The kinetic data of a polymerization run was obtained by measuring the pressure drop of monomer against time using mercury manometer on the gas line. The amount of monomer being consumed during the reaction was calculated from the ideal gas law,  $\Delta n = (\Delta P \times V) / RT$

where  $\Delta P$  is the pressure drop,  $V$  refers to the constant volume, 2997 mL,  $R$  is the Universal gas constant and  $T$  is the monomer gas temperature which was presumed as room temperature. The catalytic activity of a polymerization run is expressed as the amount of polymer formed per g of Cr per hour per 1 atmosphere monomer pressure. Figure 1 shows the plot of catalytic activity versus time for ethylene polymerization. Chromium(III) monochloroacetate,  $[\text{Cr}_3\text{O}(\text{ClCH}_2\text{COO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot 3\text{H}_2\text{O}$  catalyst system was used where %Cr = 17.25%. 0.0197 g chromium complex was mixed with 87 mL toluene and 13 mL diethylaluminium chloride as cocatalyst. The Al/Cr ratio was 30.8. The mixture were left to 'age' for 15 min. Polymerization was then carried out at room temperature for 60 min. The kinetic curve obtained was of the decay type (Keii 1972). The catalytic activity decreased rapidly to a constant value after a few minutes the reaction started. Second decay happened

after 10 min of the stationary state. The rate declined at a slower pace. This further decrease might be due to the polymer accumulated around the polymerization active center thus deactivated the catalyst. As the polymerization time increases, the decline in rate becomes smaller (Boor 1979). Varying the catalyst-monomer system would result in different rate of decline. Other factors that lead to the decrease in polymerization activity include a decrease in number of active centers and a lowering in activity of individual centers due to structural changes.

The effect of diethylaluminium cocatalyst to catalyst ratio was investigated by carrying out polymerization run at various Al/Cr ratios varied from 20.8 to 42.2. The dependence of the catalytic activity on Al/Cr ratio is illustrated in Figure 2. Optimum activity was achieved with Al/Cr ratio 30.8 where the maximum catalytic activity approached 1768 gPE/gCr/hr/atm. Drop in maximum

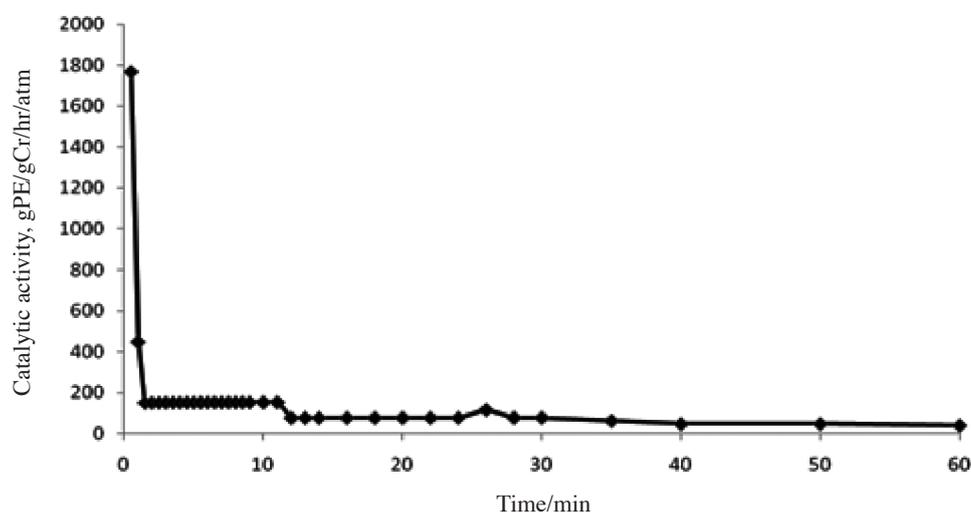


FIGURE 1. Kinetic curve of ethylene polymerization using  $[\text{Cr}_3\text{O}(\text{ClCH}_2\text{COO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot 3\text{H}_2\text{O}/\text{AlEt}_2\text{Cl}$  catalyst system at Al/Cr molar ratio= 30.8, temperature= 29°C, aging time= 15 min, reaction time= 60 min, solvent= toluene

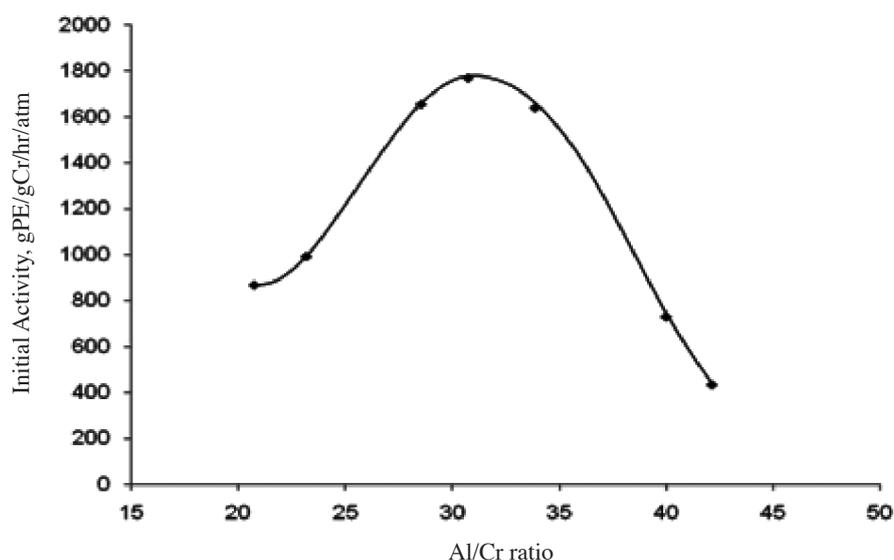


FIGURE 2. Plot of maximum initial activity versus Al/Cr ratio using  $[\text{Cr}_3\text{O}(\text{ClCH}_2\text{COO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot 3\text{H}_2\text{O}/\text{AlEt}_2\text{Cl}$  catalyst system at 29°C, aging time= 15 minutes, reaction time= 60 minutes, solvent= toluene

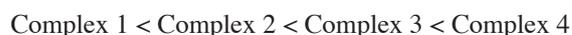
initial activity was observed as the molar ratio of Al/Cr decreases from 30.8 to 20.8. Lowering in the catalytic activity probably due to incomplete activation of the active centers. For polymerization at low Al/Cr molar ratio of 20.8, the reaction only occurred for 40 min. No further drop in monomer pressure was observed from then on until the end of the run. This might be due to insufficient concentration of aluminium alkyl needed to activate the catalyst centers. Polymerization activity would also decrease if the Al/Cr molar ratio is larger than 30.8. McKenzie et al. (1972) suggested that as the concentration of aluminium alkyls increases, transfer reactions become more significant and there is a possibility of a reversible active centers deactivation by adsorption of free aluminium alkyls. Besides, if the alkyl aluminium used is in excess with respect to the molar concentration of active centers, it might over reduce Cr to lower oxidation state and lead to decrease in activity.

Reaction temperature plays an important role in the polymerization of ethylene and propylene (Combs et al. 1967; Keii et al. 1982). A number of ethylene polymerization runs were carried out at different reaction temperatures ranging from 18 to 40°C to study the rate of polymerization affected by the temperature. The catalytic activity rose substantially with an increase in the polymerization temperature from 18 to 29°C. This is due to the steady state of polymerization increased with temperature. Figure 3 illustrates the kinetic curves of ethylene polymerization at various temperatures. The maximum rate obtained was 1768 gPE/gCr/hr/atm and 0.32 g polymer was yielded. Further increase in temperature led to a drop in the activity of catalyst. Polymerization of ethylene at temperature 36°C and 40°C showed lower activity than that at 29°C. This phenomenon was explained by Keii et al. (1968) that an irreversible decrease in the number of polymerization centers happened with increasing temperature. Comparison

between polymerization activity at 29°C and 40°C was shown in Figure 4.

Different ligands attached to the transition metal could vary the properties of the catalyst thus changes the polymerization rate. Effect of chloro-substituent groups on chromium(III) carboxylate complexes were studied by carrying out ethylene polymerization using different chromium(III) complexes synthesized by reacting commercial chromium(III) nitrate nonahydrate salt with different chloro-substituted carboxylic acids. Al/Cr molar ratio was maintained constant between 29-30 and mixture of catalyst and cocatalyst was allowed to react for 15 minutes before introducing ethylene monomer. Data obtained are summarized in Table 4.

Figure 5 shows the plots of maximum initial activity versus time for the catalysts. All four catalyst systems show decay-type kinetic curves. Ethylene polymerization using chromium(III) trichloroacetate complex,  $[\text{Cr}_3\text{O}(\text{Cl}_3\text{CCOO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot 2\text{H}_2\text{O}$  showed the highest activity among all other catalysts. The maximum initial activity increased as the number of chlorine atom in the complex increases. This is attributed to the electron withdrawing effect of the chlorine atoms (Tjaden & Jordan 1994). Same observation was reported by Tajima and Kunioka (1968) on the polymerization of ethylene using  $\text{Ti}(\text{NMe}_2)_n\text{Cl}_{4-n}/\text{AlEt}_3$  systems. The order in increasing activity of the chloro-substituted carboxylate complexes in this study is as follows:



where

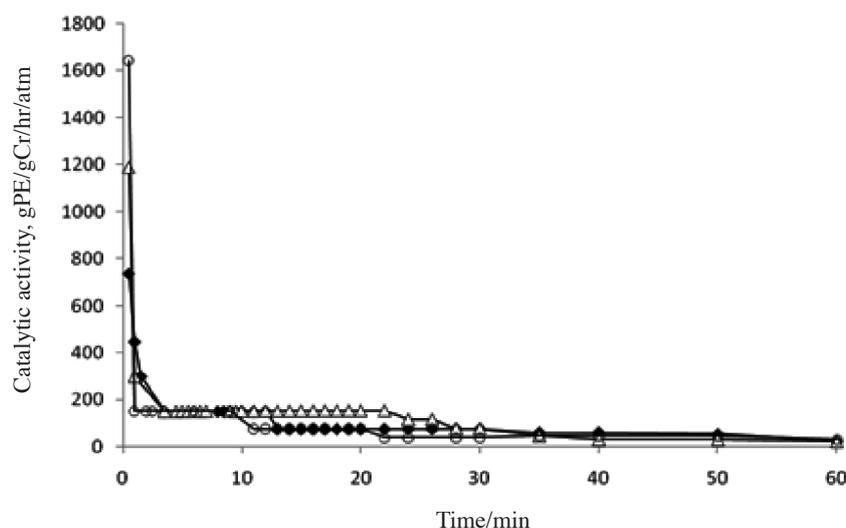
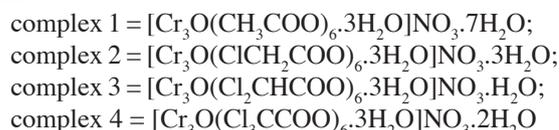


FIGURE 3. Kinetic curves of ethylene polymerization at various temperatures using  $[\text{Cr}_3\text{O}(\text{ClCH}_2\text{COO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot 3\text{H}_2\text{O}/\text{AlEt}_2\text{Cl}$  catalyst system, aging time= 15 minutes, reaction time = 60 minutes, solvent = toluene, temperatures:  $\circ$ , T= 18°C;  $\triangle$ , T= 22°C;  $\bullet$ , T= 36°C

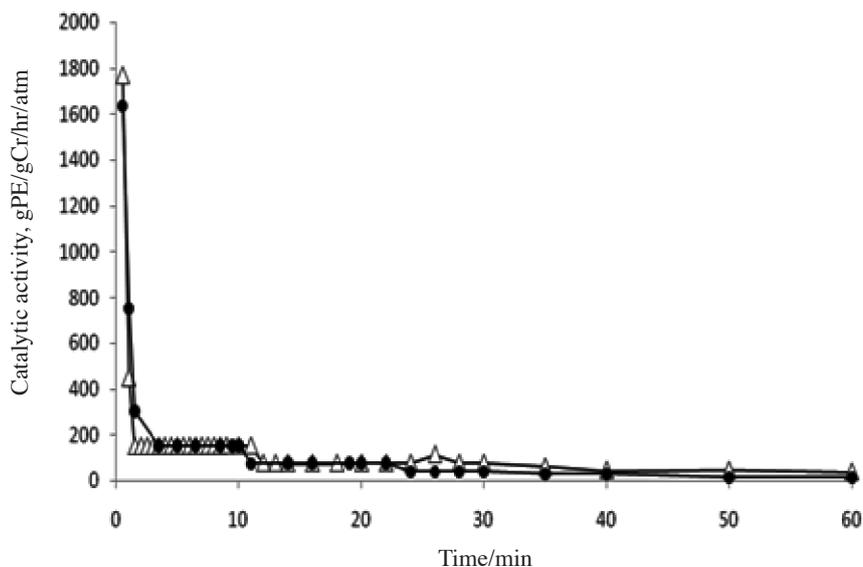


FIGURE 4. Kinetic curves of ethylene polymerization at various temperatures using  $[\text{Cr}_3\text{O}(\text{ClCH}_2\text{COO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot 3\text{H}_2\text{O}/\text{AlEt}_2\text{Cl}$  catalyst system, aging time= 15 min, reaction time= 60 min, solvent= toluene, temperatures:  $\Delta$ , T= 29°C;  $\bullet$ , T= 40°C

TABLE 4. Catalytic activity and polyethylene yield obtained using a series of chromium(III) carboxylate complexes

Catalyst	Al/Cr ratio	Maximum Initial Activity/ gPE/gCr/hr/atm	Yield/ g
$[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot 7\text{H}_2\text{O}$	29.3	1057	0.32
$[\text{Cr}_3\text{O}(\text{ClCH}_2\text{COO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot 3\text{H}_2\text{O}$	29.8	1548	0.49
$[\text{Cr}_3\text{O}(\text{Cl}_2\text{CHCOO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot \text{H}_2\text{O}$	29.6	1573	0.57
$[\text{Cr}_3\text{O}(\text{Cl}_3\text{CCOO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot 2\text{H}_2\text{O}$	29.8	3116	0.54

Polymerization conditions: Cocatalyst =  $\text{AlEt}_2\text{Cl}$ , gas temperature = 29°C, reactor temperature = 29°C, aging time = 15 minutes, reaction time = 60 minutes, volume = 2997 ml, solvent= toluene

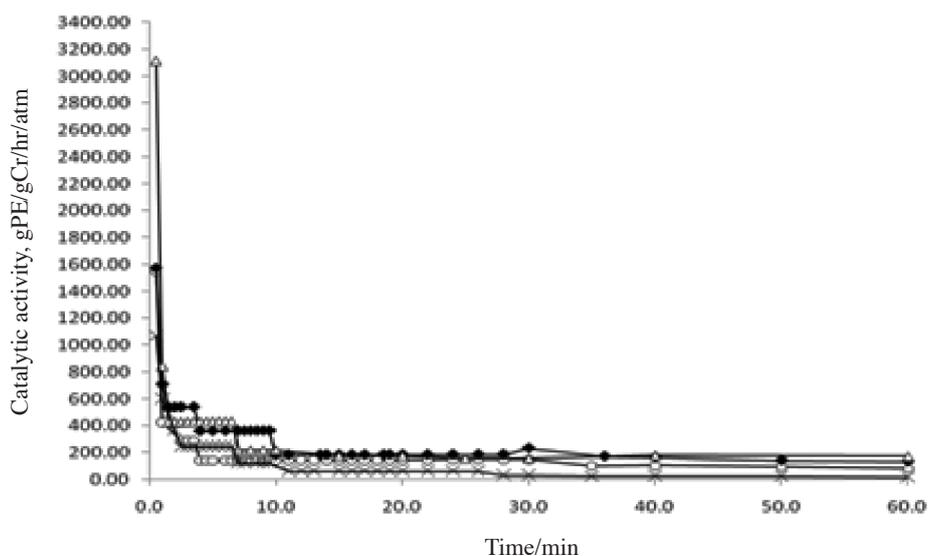


FIGURE 5. Kinetic curves of ethylene polymerization using different chromium(III) catalysts:  $\Delta$ ,  $[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot 7\text{H}_2\text{O}$ ;  $\bullet$ ,  $[\text{Cr}_3\text{O}(\text{ClCH}_2\text{COO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot 3\text{H}_2\text{O}$ ,  $\square$ ,  $[\text{Cr}_3\text{O}(\text{Cl}_2\text{CHCOO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot \text{H}_2\text{O}$ ;  $\circ$ ,  $[\text{Cr}_3\text{O}(\text{Cl}_3\text{CCOO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot 2\text{H}_2\text{O}$

Figure 6 shows the infrared spectrum of a polyethylene sample polymerized at Al/Cr ratio 23.2. The bands appeared at 2915 and 2848  $\text{cm}^{-1}$  are assigned to asymmetric and symmetric  $\text{CH}_2$  stretching mode (Fox & Martin 1940). Absorption band at 1473  $\text{cm}^{-1}$  was due to deformation of the  $\text{CH}_2$  groups in the molecules. Splitting of the peak was observed in every spectrum. Absorption band at 1367  $\text{cm}^{-1}$  indicates the symmetric terminal  $\text{CH}_3$  deformation (Tschamler 1954). This band appeared weak in most of the spectrum. For polyethylene produced at Al/Cr 42.2,  $\delta_s(\text{CH}_3)$  is observed at 1377  $\text{cm}^{-1}$ . Strong bands in the 731-717  $\text{cm}^{-1}$  region indicates the methylene rocking mode (Sheppard & Sutherland 1947). The crystallinity content of polyethylene samples was determined by calculating the absorbance ratio at 730 and 720  $\text{cm}^{-1}$ . Table 5 summarizes the crystallinity of polyethylene obtained at various Al/Cr molar ratio. All the PE samples showed absorption ratio around 1.00 reflects that the crystallinity of polyethylene produced was generally high. At Al/Cr

ratio of 42.2, the absorption frequency at 730  $\text{cm}^{-1}$  is more intense than the 720  $\text{cm}^{-1}$ . This indicates that the polyethylene obtained from Al/Cr molar ratio of 42.2 is more crystalline compared with those obtained at lower Al/Cr molar ratio.

All the polyethylene samples display well defined endotherms with high melting temperature range between 129-136°C indicating the samples are highly crystalline. The melting peak increases slightly during second heating after annealing the samples at 35°C for 5 min. At higher  $\text{AlEt}_2\text{Cl}$  concentration, lower melting temperature was obtained. Decrease in melting point was observed as the Al/Cr ratio increases which imply a decrease in crystal perfection. In the cooling scan, a sharp and well-defined crystallization peak with minimum temperature 118°C was obtained. This indicated the ethylene units in the polymer chain were able to align and crystallize. Enthalpy of fusion reflects the amount of crystallinity in a polymer sample. The literature value for the enthalpy change of

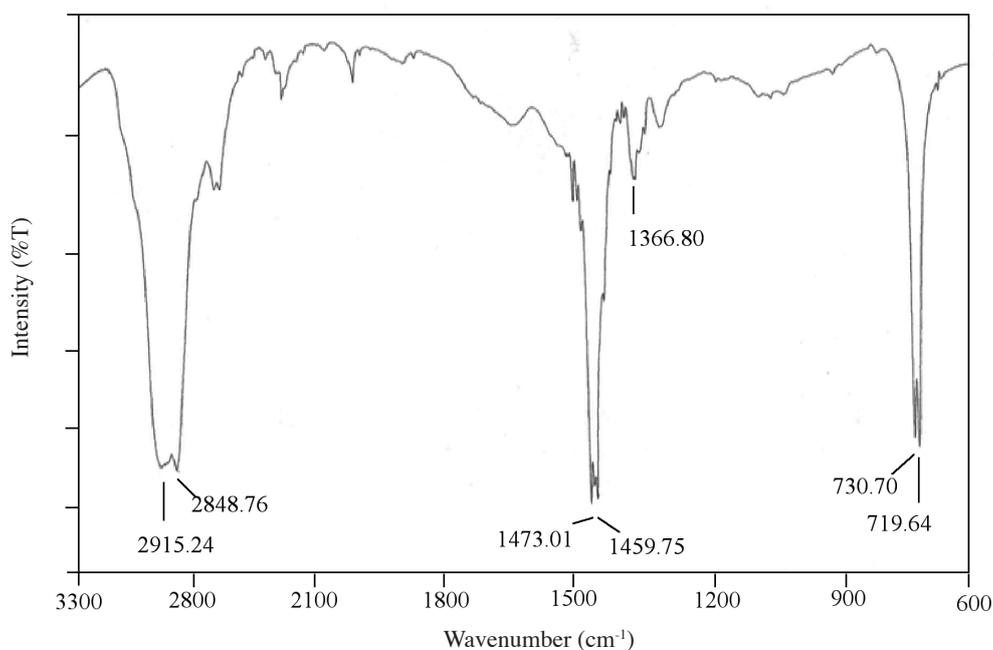


FIGURE 6. FT-IR spectrum of polyethylene obtained from  $[\text{Cr}_3\text{O}(\text{ClCH}_2\text{COO})_6 \cdot 3\text{H}_2\text{O}] \text{NO}_3 \cdot 3\text{H}_2\text{O} / \text{AlEt}_2\text{Cl}$  catalyst system at Al/Cr molar ratio 23.2

TABLE 5. FT-IR band assignments of polyethylene obtained at various Al/Cr molar ratios

Polyethylene vibration mode ( $\text{cm}^{-1}$ )	Al/Cr ratio					
	23.2	30.8	31.2	40.0	42.2	
$\text{CH}_2$ -stretching	Asymmetric	2915 s	2908 s	2922 s	2915 s	2918 s
	Symmetric	2848 s	2845 s	2851 s	2849 s	2849 s
$\text{CH}_2$ -deformation		1473 s	1474 s	1474 s	1473 s	1472 s
		1460 s	1463 s	1463 s	1464 s	1463 s
Symmetric terminal $\text{CH}_3$ -deformation		1367 w	1367 w	1367 w	1364 w	1377 w
$\text{CH}_2$ -rocking		731 s	730 s	731 s	730 s	730 s
		720 s	720 s	719 s	720 s	720 s

Abbreviations: s = strong; w = weak

TABLE 6. DSC measurements of polyethylene at various Al/Cr molar ratios

Al/Cr Ratio	First Heating			Cooling			Second Heating		
	T <sub>m</sub> /°C	T <sub>o</sub> /°C	ΔH/J/g	T <sub>c</sub> /°C	T <sub>o</sub> /°C	-ΔH/J/g	T <sub>m</sub> /°C	T <sub>o</sub> /°C	ΔH/J/g
23.2	136	126	200	118	121	181	136	124	197
30.8	133	123	199	118	121	179	134	123	196
31.2	133	122	202	118	121	182	134	122	199
40.0	133	122	200	118	120	181	134	122	198
42.2	129	120	208	117	119	191	131	120	209

a single crystal of polyethylene is 293 J/g (Wunderlich 1990). Enthalpy values obtained during second heating range from 199 J/g to 208 J/g implied that the polyethylene samples produced in this study were 68-71% crystalline. The ΔH value for polyethylene prepared at Al/Cr molar ratio 42.2 is the highest among all samples indicated that its crystallinity is the highest. This is in well agreement with A<sub>730</sub>/A<sub>720</sub> results obtained from infrared analysis. Table 6 summarizes the DSC readings of polyethylene at various Al/Cr molar ratios.

#### CONCLUSIONS

The heterogenous [Cr<sub>3</sub>O(CICH<sub>2</sub>COO)<sub>6</sub>.3H<sub>2</sub>O]NO<sub>3</sub>.3H<sub>2</sub>O/AlEt<sub>2</sub>Cl catalyst system in toluene solvent showed polymerization activity for ethylene. The polymerization activity is largely dependent on the molar ratio of cocatalyst to catalyst and reaction temperature. Besides, the electron withdrawing power of chlorine atoms in the complexes would also affect the catalytic activity. Characteristic bands of polyethylene were shown in all FT-IR spectra. All PE samples were highly crystalline with melting temperatures and crystallization temperatures around 129-136°C and 118°C, respectively.

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